

*Sergiy Mudryy, Viktor Reutskyy, Oleksandr Ivashchuk,
Oleksandr Suprun and Volodymyr Ivasiv*

INFLUENCE OF ORGANIC ADDITIVES ON CATALYSTS OF LIQUID-PHASE CYCLOHEXANE OXIDATION

*Lviv Polytechnic National University,
12, St. Bandera str., 79013 Lviv, Ukraine; mso1984tm@mail.ru*

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Abstract. Research of oxygen and nitrogen containing organic additives to the catalyst influence on the main parameters of the process of cyclohexane oxidation have been conducted. A wide range of nitrogen and oxygen containing compounds and compounds based on polyglycols with varying molecular weight have been used as additives. The obtained results have been analyzed in view of the structural features of the studied additives and the probability of their interaction with the catalyst and intermediate products of oxidation with subsequent formation of intermediate complexes or associates.

Keywords: cyclohexane, oxidation, catalysis, chelates, complex compounds.

1. Introduction

Homogeneous catalytic oxidation of cyclohexane to cyclohexanone (CON) and cyclohexanol (COL) is widely used today. These products are used as raw materials for the synthesis of polyamide fibers – nylon and kapron [1–5, 12].

Existing catalytic systems are characterized by low efficiency, which does not allow to reach high rates of conversion of raw materials for oxidation of cyclohexane. Low value of the conversion cause significant energy losses associated with the recycling of raw materials [6]. Increasing of conversion of hydrocarbons leads to a significant decrease of selectivity of the process due to the accumulation of by-products, primarily acids and ethers. Increase of selectivity and conversion values of this process by at least 1 % will significantly reduce the expense coefficients for raw materials and energy. Therefore, the creation of efficient catalytic systems for homogeneous catalytic oxidation of cyclohexane remains relevant [2, 7, 8].

It is known that the processes of hydrocarbons oxidation are passing with higher selectivity by non-chain mechanism in the coordination sphere of homogeneous catalyst. Application of additives of different nature (donors and acceptors of electrons) to cobalt naphthenate (NC) increases selectivity of the process for target products and changes the ratio between them in the required direction, which determines the direction of their future use [9-11].

There are many studies showing the effectiveness of the use of additives based on polyglycols with varying molecular weight. In their presence the selectivity of oxidation process of CyH increases by 5–10 %, and the ratio between [COL]/[CON] changes in a wide range of values. Somewhat similar results are obtained in the presence of nitrogen containing additives. In their presence threefold decrease in the concentration of acids and twofold increase in the concentration of peroxide compounds in comparison with the results obtained in the presence of NC was reached.

In view of the above results it is advisable to investigate the binary catalytic system consisting of NC and polyglycols as additives and NC with nitrogen contain additives with various donor-acceptor substituents.

2. Experimental

The process of oxidation of cyclohexane was studied at the pressure of 1.0 MPa and the temperature of 418 K in the autoclave reactor bubbling type of stainless steel (Fig. 1). Oxidation was carried out by molecular oxygen, which bubbled under pressure through a liquid phase. The concentration of NC was $5.0 \cdot 10^{-4}$ mol/l. Molar ratio [NC] / [additive] was 1:1.

At fixed intervals samples were taken from the liquid phase and analyzed by titrimetric and chromatographic methods. The main products of liquid-phase

oxidation of cyclohexane are peroxide compounds (mostly cyclohexyl hydroperoxide (CHP)), cyclohexanol, cyclohexanone, acids (mostly adipic acid (AA)) and ethers (including dicyclohexyl adipate (DCHA)). The concentrations of CO and CO₂ were not measured because their contents did not exceed the error of analysis.

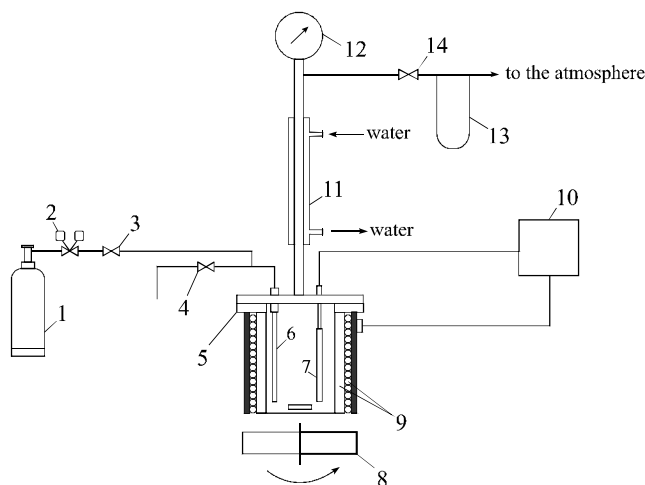


Fig. 1. Autoclave plant for oxidation of cyclohexane: oxygen cylinder (1); reducer (2); valves (3, 4, 14); electric heating reactor (9); control-measuring device (10); reactor for the oxidation of cyclohexane (5); inverse heat exchanger (11); pressure gauge (12); manometer for measuring oxygen consumption (13); magnetic stirrer (8); capillary for oxygen (6) and thermocouple (7)

The rates of the products formation are average on the interval between samplings and are calculated by the formula:

$$W = \frac{(C_{CHP}^{t_2} + C_{AA}^{t_2} + 3C_{DCHA}^{t_2} + C_{COL}^{t_2} + C_{CON}^{t_2})}{(t_2 - t_1)} - \frac{(C_{CHP}^{t_1} + C_{AA}^{t_1} + 3C_{DCHA}^{t_1} + C_{COL}^{t_1} + C_{CON}^{t_1})}{(t_2 - t_1)}$$

where C_x^t – concentration of a specific product of oxidation of cyclohexane at time t_i ; t_i – time of sampling, which is measured from the beginning of the process of oxidation in seconds.

3. Results and Discussion

Investigation of liquid-phase homogeneous catalytic oxidation of cyclohexane in the presence of binary catalytic systems consisting of NC (as industrial catalytic systems) and additives was conducted. A wide range of nitrogen and oxygen containing compounds and compounds based on polyglycols with varying molecular weight were used as additives. The results that significantly differ from the similar ones in the presence of NC were taken for comparisons. Experimental results

were obtained in the presence of the following additives: poly(ethylene glycol) adipate (PEA4000), poly(ethylene glycol) succinate (PES4000), bis-2-cyanethyl ether (CEE), tetraethylammonium iodide (TEAI), tetrabutylammonium bromide (TBAB), and L₁L₁-(tris-betacyanethyl) acetophenone (BCAF) (Table 1).

In the process of liquid-phase oxidation the composition and properties of the reaction mixture is significantly changing. This is due to the accumulation of various oxygen containing compounds that are capable of further transformation and interaction with the catalyst, affecting its activity and selectivity. Therefore, it is reasonable to investigate the effect of additives on the values of selectivity for certain products at low conversion of raw materials ($K = 1-2\%$), and values close to industrial ($K \approx 4\%$). This will allow to analyze the dynamics of the main parameters of homogeneous catalytic oxidation of cyclohexane and incorporate the impact of products on the catalytic oxidation system.

From the analysis of the experimental data it was established that at low conversion of raw materials ($K = 1-2\%$) the average oxidation products accumulation rate is lower in the presence of the most researched additives in comparison with similar data obtained in the presence of individual NC. Thus, the average rate of accumulation of products of cyclohexane oxidation process in the presence of NC is $W = 2.908 \cdot 10^{-4}$ mol/(l·s) and in the presence of the investigated additives values of the average rate of products accumulation is in the range $W = 0.53-2.4$ mol/(l·s), except for BAB and TEAI, the use of which allowed to get 1.5–2 times higher average rate values (Table 2).

At the achievement of higher values of conversion of hydrocarbons ($K \sim 4\%$) in the presence of CEE and BCAF an increase of the average values of the rate of accumulation of oxidation products compared with individual NC is observed. It is likely that these additives to catalytic system do not participate in the formation of radical chains (with $K = 1-2\%$). However, at the deeper oxidation ($K > 4\%$) they influence the course of radical chain transformations (Table 2).

The influence on the process of oxidation of the investigated additives varies depending on their nature. At the initial stages of cyclohexane oxidation at conversion of raw materials in the range of $K = 1-2\%$ the nitrogen containing additives (CEE, TEAI, TBAB, and BCAF) led to increased concentrations of COL and CON and lower concentrations of DCHA compared with individual NC. The [COL] / [CON] ratio significantly changed toward the accumulation of ketone only in the presence of BCAF additive. Despite the high concentration of peroxide compounds, the formation of COL and CON in the presence of PES4000 was not observed (Table 3).

Table 1

Structural formulas of the investigated additives

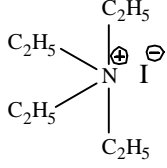
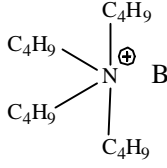
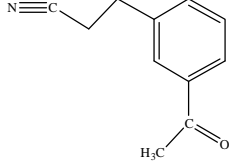
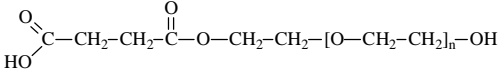
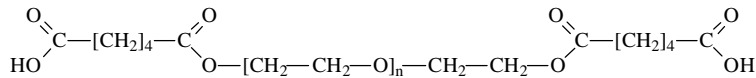
		
Tetraethylammonium iodide	Tetrabutylammonium bromide	L ₁ L ₁ -(tris-betacyanethyl) acetophenone
$N \equiv C - CH_2 - CH_2 - O - CH_2 - CH_2 - C \equiv N$		
Bis-2-cyanethyl ether	Polyethyleneglycol succinate (M ≈ 4000 g/mol)	
		
Poly(ethylene glycol) adipate (M ≈ 4000 g/mol)		

Table 2

The average rate of accumulation of products of liquid-phase oxidation of cyclohexane at conversion close to 2 and 4%. $C(\text{NC}) = 5.0 \cdot 10^{-4}$ mol/l. Molar ratio $[\text{NC}] / [\text{additive}] = 1:1$

Catalytic systems	$K \sim 2\%$	$K \sim 4\%$
	$W \cdot 10^4, \text{ mol}/(\text{l} \cdot \text{s})$	$W \cdot 10^4, \text{ mol}/(\text{l} \cdot \text{s})$
NC	2.908	4.638
NC + PEA4000	2.400	4.033
NC + PES4000	0.533	2.633
NC + CEE	1.454	5.404
NC + TEAI	3.292	3.257
NC + TBAB	4.522	3.677
NC + BCAF	1.109	5.578

Table 3

Selectivity of cyclohexane oxidation process in the presence of additives at conversion of raw materials $K = 1-2\%$. $C(\text{NC}) = 5.0 \cdot 10^{-4}$ mol/l. Molar ratio $[\text{NC}] / [\text{additive}] = 1:1$

Catalytic systems	$S_{AA}, \%$	$S_{DCHA}, \%$	$S_{CHP}, \%$	$S_{COL}, \%$	$S_{CON}, \%$	$[\text{COL}]/[\text{CON}]$
NC	12.5	11.6	18.5	40.7	16.7	2.4
NC + PEA4000	16.7	0.0	26.7	56.6	0.0	–
NC + PES4000	26.7	11.4	73.3	0.0	0.0	–
NC + CEE	7.2	11.8	28.1	33.3	19.5	1.7
NC + TEAI	2.2	47.5	6.9	24.6	18.8	1.3
NC + TBAB	7.5	35.0	18.7	25.4	13.4	1.9
NC + BCAF	7.9	34.7	18.6	18.8	20.0	0.9

Notes: S_{AA} – selectivity of acids, %; S_{CHP} – selectivity of peroxide compounds, %; S_{DCHA} – selectivity of ethers, %; S_{COL} and S_{CON} – selectivities of cyclohexanol and cyclohexanone, respectively, %.

Selectivity of cyclohexane oxidation process in the presence of additives at conversion of raw materials
 $K \sim 4 \%$. $C(\text{NC}) = 5.0 \cdot 10^{-4}$ mol/l. Molar ratio $[\text{NC}] / [\text{additive}] = 1:1$

Catalytic systems	$S_{AA}, \%$	$S_{DCHA}, \%$	$S_{CHP}, \%$	$S_{COL}, \%$	$S_{CON}, \%$	$[\text{COL}]/[\text{CON}]$
NC	15.7	15.9	5.1	42.9	20.3	2.1
NC + PEA4000	26.1	4.9	6.5	41.2	21.4	1.9
NC + PES4000	16.6	13.0	10.8	38.7	20.9	1.9
NC + CEE	18.8	7.5	6.8	41.6	25.3	1.6
NC + TEAI	5.73	29.6	8.9	36.3	19.5	1.9
NC + TBAB	10.6	25.5	12.7	36.6	14.6	2.5
NC + BCAF	10.8	19.8	11.0	39.5	18.9	2.1

The most effective additive is CEE at conversion of raw materials close to industrial values ($K \approx 4 \%$). In its presence twice as lower selectivity of ethers ($S_{DCHA} = 7.5 \%$) was obtained while increasing selectivity of COL and CON by 1 and 5 %, respectively, compared with the individual NC (Table 4).

The following additives had a similar catalytic effect on the oxidation of cyclohexane: TEAI, TBAB, and BCAF. The results differed significantly only by the selectivity of acids and ethers.

It should be noted that the additives of polyglycolic series, in particular PEA4000 and PES4000 allowed to retain selectivity of COL and CON close to the values obtained in the presence of individual NC, while changing the ratio between acids, ethers, and peroxide compounds. Thus, the addition PEA4000 allowed to get the highest selectivity of acids ($S_{AA} = 26.1 \%$) and the lowest one of ethers ($S_{DCHA} = 4.9 \%$). The presence of PES4000 leads to higher selectivity of ethers ($S_{DCHA} = 13.0 \%$) and peroxide compounds ($S_{CHP} = 10.8 \%$) compared with NC (Table 4).

The difference in the character of influence of additives on the cyclohexane oxidation process at low and high values of the conversion of raw materials is due to the fact that at prolonged oxidation oxygen containing intermediate products are present in the reaction mixture, which also react with the catalytic system and affect its activity.

Catalytic influence of nitrogen containing additives is associated with the presence of the $-\text{C}\equiv\text{N}$, $-\text{COR}$ groups and halogens that exhibit electrophilic properties. This leads to a shift of the electron cloud to their side, which can greatly affect the coordination of variable valence metal (cobalt) during the formation of the active complex [8].

Investigation of infrared absorption spectra of created model compounds to identify new chemical bonds and formation of complexes between CEE (as the most effective additive, given the highest selectivity for COL and CON) and NC was conducted. CON was used as a solvent since it is present in the reaction mixture in the

process of oxidation, and NC dissolves better compared with cyclohexane and COL.

Increasing intensity of absorption in the region $\delta = 3560\text{--}3500 \text{ cm}^{-1}$ may indicate the formation of intermolecular hydrogen bonds with polar compounds, namely the polar additive CEE (Fig. 2). Intensified absorption at frequencies $\delta = 3250, 3160, \text{ and } 3100 \text{ cm}^{-1}$ indicates the complexation involving $-\text{OH}$ groups of naphthenic acids contained in NC, and $-\text{C}\equiv\text{N}$ group comprising additive CEE. The band at 2070 cm^{-1} indicates the presence of free $-\text{C}\equiv\text{N}$ groups contained in CEE; in the spectra of $[\text{NC} + \text{CON}]$ this band is absent⁹ (Fig. 2).

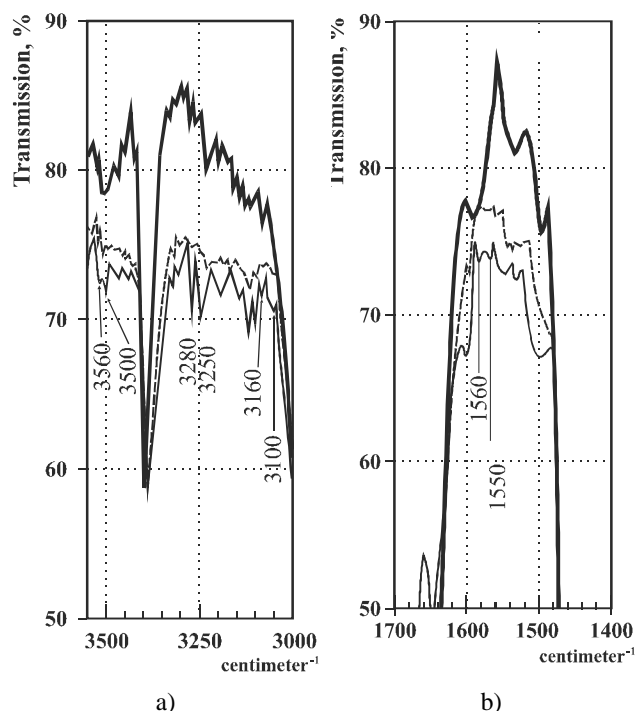


Fig. 2. IR- spectra of the prepared catalytic systems in cyclohexanone

NC+CON ———
 CON+CEE - - - -
 NC+CON+CEE ———

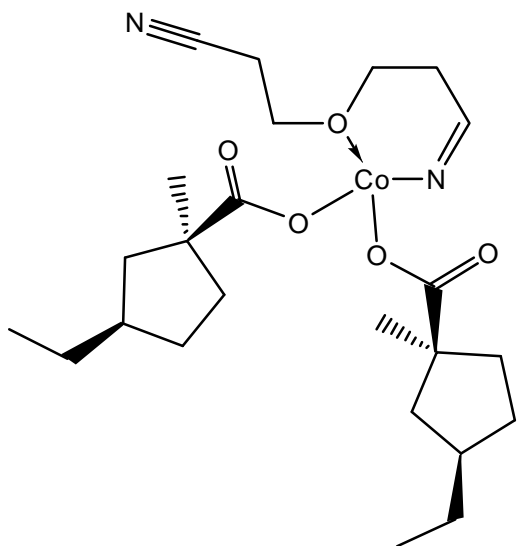


Fig. 3. Probable structural model of compound formed in the reaction mixture in the presence of cobalt naphthenate and nitrogen containing additive of bis-2-cyanethyl ether in ketone environment

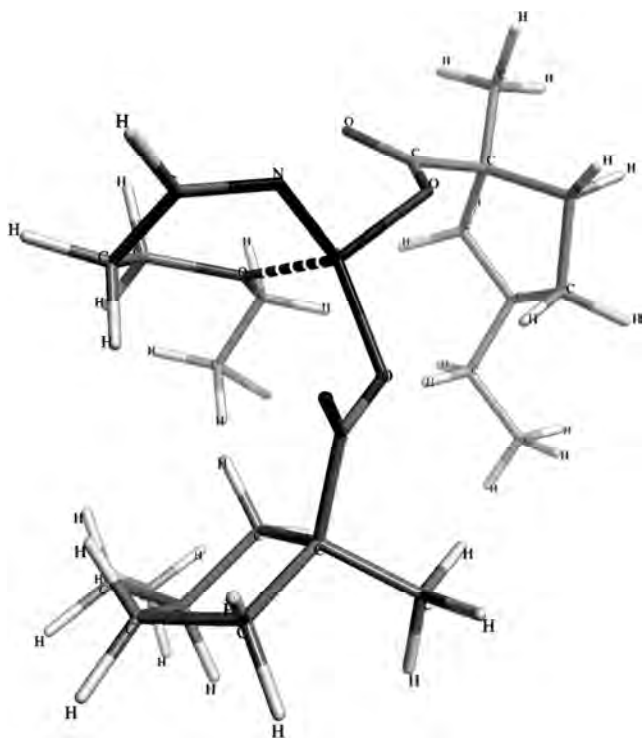


Fig. 4. Spatial 3D model of the most likely compound formed in the reaction mixture in the presence of cobalt naphthenate and nitrogen containing additive of bis-2-cyanethyl ether in ketone environment

Enhanced absorption in the frequencies $\delta = 1550$ and 1560 cm^{-1} indicates the formation of chelate bonds between NC and CEE with group $-\text{C}\equiv\text{N}$ and acid $-\text{C}=\text{O}$ groups, respectively. It should be noted that the appearance of the aforementioned bands was observed only in the model solution [CON + NC + CEE] and not in [NC + CON] and [CEE + CON], indicating the interaction of NC and CEE with CON.

Summarizing the above IR spectra research results of the created model system within NC CON and CEE an approximate structural model of compound that can be formed in the reaction mixture has been built (Fig. 3).

Using modern computer technology and numerous calculations we managed to build an illustrative spatial 3D model of the above complex compound, which takes into account bonds energy and different steric factors that influence the spatial location of individual groups of substituents in the molecule (Fig. 4).

4. Conclusions

The effectiveness of nitrogen containing compounds and polyglycols as additives to the catalytic oxidation process of cyclohexane has been confirmed based on the experimental data.

Effect of cobalt naphthenate catalytic activity change under the influence of the studied additives has been grounded by the research results of IR-absorption spectra of the created model solutions. Thanks to modern methods using computer technology we managed to build the most probable structural formula of the newly created catalytic complex consisting of cobalt naphthenate and bis-2-cyanethyl ether.

Experimental data extend the general understanding of the influence of oxygen and nitrogen containing additives on the homogeneous catalytic oxidation process of cyclohexane and allow to create new effective catalytic system more predictably.

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ВПЛИВ ОРГАНІЧНИХ ДОДАТКІВ НА КАТАЛІЗАТОРИ ПРОЦЕСУ РІДИННОФАЗНОГО ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

Анотація. Досліджено вплив кисне- та азотовмісних органічних додатків до каталізатора на склад та співвідношення продуктів окиснення циклогексану. Як добавки використовували широкий спектр азотовмісних та кисневмісних речовин з різною молекулярною масою. Одержані результати проаналізовано з огляду на особливості будови досліджуваних додатків, та ймовірності їх взаємодії з каталізатором і проміжними продуктами окиснення з подальшим утворення проміжних комплексів чи асоціатів.

Ключові слова: циклогексан, окиснення, каталіз, хелати, комплексні сполуки.